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(71) Applicant *(for all designated States except US)*: NUVERA FUEL CELLS, INC. [US/US]; 35 Acorn Park, Cambridge, MA 02140 (US).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: SHI, Yanlong [CN/US]; 147 King Street, Apt. 506, Littleton, MA 01460 (US).

(74) Agents: SMITH, James, M. et al.; Hamilton, Brook, Smith & Reynolds, P.C., 530 Virginia Road, P.O. Box 9133, Concord, MA 01742-9133 (US).

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(54) Title: PROTECTION OF REDUCED CATALYSTS IN STREAM REFORMING AND WATER GAS SHIFT REACTIONS

(57) Abstract: Many catalysts for steam reforming and the water gas shift are required to be in the reduced form, and can be inactivated by trace oxygen in feeds of fuel or steam. Inactivation of such catalysts by oxygen can be prevented by placing an oxygen-consuming catalyst at or near the inlet end of the reduced catalyst bed, so that any oxygen entering the bed will be reacted with fuel or reformate before reaching the reduced catalyst. This increases the durability of the reduced catalyst.

PROTECTION OF REDUCED CATALYSTS IN STEAM REFORMING AND WATER GAS SHIFT REACTIONS

RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 60/362,792, filed March 8, 2002, the entire teachings of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

The steam reforming reaction is well known. In this reaction, a gaseous fuel, typically a hydrocarbon or an alcohol, is mixed with steam at elevated temperature, usually in the presence of a catalyst. The fuel and water are converted into hydrogen and carbon monoxide. Using methane as an example, the "reforming" reaction is:

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

In subsequent reactions the CO (carbon monoxide) is usually reacted with more water to form CO_2 (carbon dioxide) and H_2. This is called the "water gas shift" reaction, or "shift" reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The resulting hydrogen-containing gas, generally called the reformate, is used for any of several purposes, but particularly for the generation of electricity using a fuel cell.

The steam reforming reaction is endothermic (absorbs heat), and so heat must be supplied to the system to drive the reaction. In "pure" steam reforming,

here also called simply "steam reforming" unless qualified, the heat is supplied from an outside source to the catalyst bed. There are other forms of steam reforming, most commonly called "autothermal reforming" and "partial oxidation reforming", in which some of the fuel is burned in the bed to create the heat required for reforming the fuel. Autothermal reforming and partial oxidation reforming each require oxygen-resistant catalysts, since oxygen is admitted to the catalyst bed. If oxygen has to be present, then a noble metal catalyst, such as platinum, is usually required, and efficient catalysts have been developed for such reactions. However, it is not generally economical to use the more expensive noble metals in a reaction, such as a "pure" steam reforming or water gas shift reaction, that can be performed on a relatively inexpensive transition metal.

In the case of steam reforming, the catalyst used is typically a non-noble transition metal, such as Ni (nickel), or combinations comprising non-noble transition metals. In order to be effective, at least some of the Ni or other transition metal catalyst surface must be in a reduced state (e.g., Ni) rather than in an oxidized state such as NiO. This is typically achieved by pretreatment of the catalyst with hydrogen at a high temperature, for example above 500 degrees C; the exact conditions depend on the detailed composition of the catalyst. The reduced catalyst is sensitive to oxygen, meaning that oxygen will react with the reduced-state metal and oxidize it to a higher oxidation state, frequently resulting in the addition of oxygen to the catalyst complex. Hence, in actual operation, the reduced Ni-type catalyst is subject to poisoning by traces of oxygen in the feed, whether fuel, steam, or trace air leakage. This results in a loss of catalytic efficiency of the bed, and eventually the catalyst must be regenerated. Such regeneration is not unduly difficult in a large, fixed chemical plant. However, regeneration is much more difficult in a mobile reformer, for example in a vehicle, or in a small reformer at a non-industrial site, such as in a distributed electric power generating system.

The water gas shift (WGS) reaction is typically run in two stages, a HTS (high temperature shift) stage for fast kinetics, and a LTS (low temperature shift) stage to take advantage of the more favorable equilibrium (lower equilibrium CO level) at lower temperatures. The catalysts used for the water gas shift reaction are

also typically made of reduced or partially reduced transition metals and their oxides, most commonly Fe and Cr for the HTS and Cu and Zn for the LTS. Other metals, including for example Co, Mo, Mn, Zr, Ti and lanthanides, are sometimes used as the main catalyst or as part of a mixed-metal catalyst. Like the reduced steam reforming catalysts, the catalysts used for water gas shift reaction are also subject to deactivation by oxygen. Moreover, since additional steam or water is usually added between the steam reforming step and the water gas shift step(s), elimination of oxygen in or before the reforming catalyst bed may not be sufficient to protect the shift reactor bed(s) from exposure to oxygen.

SUMMARY OF THE INVENTION

We have found an effective and inexpensive remedy for the problem of inactivation of reduced catalysts used in steam reforming and water gas shift reactions (collectively, reduced reforming & shift, or RRS, catalysts). The remedy substantially lessens the degree of oxygen poisoning, and is suitable for use in small or mobile steam reformers. To prevent oxygen poisoning of a RRS catalyst, a small quantity of an oxygen-resistant catalyst that will support reaction of oxygen with the fuel or reformate is positioned in a first bed. The first bed is positioned "in front of", i.e. upstream of, a second bed containing the reduced catalyst, so that reactants must flow over the oxygen-resistant catalyst before entering the reduced bed. The two beds may be adjacent, connected in series, or may be regions of the same enclosure. The catalyst supporting oxidation of fuel or reformate can potentially be any catalyst that accelerates the rate of reaction of oxygen with a hydrocarbon, an alcohol, hydrogen, or carbon monoxide, (collectively, "fuel") and that is not poisoned by oxygen. A broad range of catalysts that catalyze the oxidation of a fuel in the presence of oxygen are known ("oxidation catalysts") and the individual suitability of catalysts for this function can easily be tested. With a suitable oxidation catalyst, trace oxygen in the feeds will react with the fuel to form carbon monoxide or carbon dioxide, and so no oxygen will be present downstream of the oxidizing catalyst. This will prolong the useful life (before regeneration is needed) of the reduced steam reforming or water-gas shift (RRS) catalyst.

A catalyst system of the invention comprises a first catalyst bed in fluid communication with a reactant feed, the first catalyst bed comprising a first catalyst that catalyzes an oxygen-consuming reaction in the reactant feed, the first catalyst being present in an amount sufficient to remove substantially all oxygen from the reactant feed before the feed exits the first catalyst bed; and a second catalyst bed configured to receive the feed from the first catalyst bed, the second catalyst bed comprising an oxygen-sensitive catalyst that promotes a hydrogen-producing reaction in the reactant feed. The hydrogen-producing reaction can be, for example, a steam reforming reaction, or a water gas shift reaction. The first catalyst can be an oxidation catalyst, such as a noble metal, including, for example, Ru, Rh, Pd, Ir, Au and Pt. The second oxygen-sensitive catalyst can be a reduced catalyst, such as a transition metal, and can comprise for example Cr, Mn, Fe, Co, Ni, Cu, Zn, and V. In addition to these widely used elements, a wide variety of other elements have been proposed or tested for use as a reduced reforming or water gas shift catalyst, and could also benefit from improved oxygen removal. The second catalyst is "oxygen-sensitive" because exposure of the catalyst to oxygen at elevated temperatures diminishes its capacity to catalyze a hydrogen-producing reaction. In this context, a "reduced" or "oxygen-sensitive" catalyst is one that is not in its highest oxidation state. By way of example, FeO (ferrous oxide) is reduced compared to Fe_2O_3 (ferric oxide). The first, upstream catalyst thus "protects" the second downstream catalyst by removing substantially all oxygen from the reactant feed, thereby preventing deactivation of the second catalyst by oxygen exposure.

In another aspect, the invention relates to a method of producing a hydrogen-containing reformate from a reactant feed, comprising flowing the reactant feed over a first catalyst bed containing a first catalyst that catalyzes an oxygen-consuming reaction in the reactant feed to remove substantially all oxygen from the reactant feed before the feed exits the first catalyst bed; and flowing the reactant feed over a second catalyst bed containing an oxygen-sensitive catalyst that catalyzes a hydrogen-producing reaction to produce a hydrogen-containing reformate.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

Figure 1a is a schematic illustration of a fuel processing system of the prior art; and

Figure 1b is a schematic illustration of a fuel processing system according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

A description of preferred embodiments of the invention follows.

Figures 1a and 1b show, in comparison, a fuel processing system of the prior art with a fuel processing system employing a catalyst system of the present invention. In Figure 1a, a conventional fuel processing system is shown schematically. A steam reforming module 1 comprises an inlet 3 for fuel and steam, a container 5 enclosing a catalyst bed 7 of a reduced steam reforming catalyst, and an outlet 10 for the products of the reforming reaction–i.e. the reformate. The catalyst 7 may be in any convenient form, including pellets, foams, and monolithic pieces. The reformer is heated by an external heat source (not shown) in order to provide energy for the reforming reaction.

The reformate passes through outlet 10 and is optionally joined by a feed line 12 carrying additional steam. The reformate, with any additional steam, enters water gas shift module 11 at inlet 13. Shift module 11 comprises a housing 14, a catalyst bed 16 of a reduced shift catalyst, and an outlet 18. The shift catalyst may be for a high temperature shift reaction, or a low temperature shift reaction, or both. In the latter case, the catalyst bed and the housing will typically be arranged to allow a downstream portion of the catalyst to be operated at a lower temperature.

A fuel processing system employing a catalyst system of the present invention is shown schematically in Figure 1b. Steam reforming module 21 includes a container 5, reduced reforming catalyst bed 7, fuel and steam inlet 3, and reformate outlet 10. In addition, an oxidizing catalyst bed 23 is positioned within the container between the inlet 3 and the upstream end of the reduced catalyst bed 7. The oxidizing catalyst 23 catalyzes the reaction of oxygen found in the fuel or steam with fuel or reformate (hydrogen, CO), so that substantially no oxygen reaches the reduced catalyst bed 7.

Similarly, the water gas shift module 31 has inlet 13, container 14, outlet 16, optional steam inlet 12, and reduced shift catalyst bed 16. It further comprises oxidizing catalyst bed 33, which is positioned upstream of reduced catalyst segment 16.

The improved apparatus of Fig. 1b is illustrated as having a first oxidizing catalyst bed before each of a reforming catalyst bed and a water gas shift bed. However, it may not be useful to have an initial oxidizing bed in both the reforming and water gas shift modules. For example, if no additional steam is introduced between the reformer and the shift bed, then an initial oxidizing bed may not be necessary to protect shift bed 16. Similarly, reformer 21 could be a reformer, for example either an autothermal reformer or a steam reformer, having an oxidizing catalyst and/or an oxygen resistant catalyst throughtout the bed. Then an additional oxidizing catalyst layer 33 might still be useful in the shift bed, but would not be required in the reforming bed.

The catalysts for the first and second catalyst beds can be in any convenient physical form. Most commonly, the catalysts will be pelleted, or otherwise provided in discrete granules, optionally porous, forming a conventional catalyst bed. Catalysts may also be present in monolithic (i.e., one-piece) form, for example impregnated into or coated onto metal or ceramic shapes, metal or ceramic foams, metal or ceramic honeycomb structures, or coated onto structural elements such as heat exchangers; these forms are also included in the term "bed", for the purposes of this description. The first bed of oxygen-consuming catalyst may be physically or structurally distinct from the second bed of oxygen-sensitive catalyst. Alternatively,

the two catalyst types may be placed sequentially in a single bed, whether as pellets or monoliths. The detailed physical arrangement will be determined by the engineering requirements of the particular reformer, with consideration given to relevant parameters such as space velocity, temperature, bed porosity and pressure drop, etc, as known in the chemical engineering art. Likewise, the relative proportions of the two catalyst types will be dictated to a large extent by similar considerations. The oxygen-removing first catalyst will be used in an amount sufficient to remove residual oxygen in the feeds of the particular reactor before the oxygen reaches a reduced catalyst. The amount of the first catalyst will depend on its activity and kinetics. The lowest feasible amount is generally preferred, because the oxidation catalysts typically contain noble metals, which are more expensive than the transition metals typically used in the reduced catalysts. As noted above, typically a separate oxidation catalyst protective bed or layer will be used before each of the reformer catalyst bed (unless the reformer is of the ATR or POX type) and at least the HTS section of the WGS catalyst bed.

One preferred type of suitable oxygen-consuming first catalyst is one that is used, or that could be used, for performing the autothermal reforming reaction (ATR; an "ATR catalyst") described above. If the oxygen-consuming catalyst is of the ATR type, then reforming will also occur in the catalyst, so that the catalyst will contribute to the reforming reaction even in the absence of oxygen, and the overall effectiveness of the catalyst bed will be maintained. Moreover, any combustion of oxygen will contribute useful heat to the reforming reaction. Alternatively or in addition, the oxygen-resistant catalyst can be suitable for partial oxidation steam reforming.

Most known ATR and POX catalysts ("ATR-type catalysts") contain a noble metal, or combination of noble metals. Metals from groups VIII and IB of the periodic table, such as Ru, Rh, Pd, Ir, Au and Pt, are usually present in such catalysts. To minimize expense, the ATR-type catalysts are usually supported on a less expensive material, such as a ceramic. They may also have their activity enhanced by the addition of other metals or metal oxides. Numerous potentially suitable oxygen-consuming catalysts are known in the art.

Likewise, many reduced catalysts for fuel reforming or water gas shift reactions are known. Without limitation, they usually comprise, alone or in combination, transition metals, including Cr, Mn, Fe, Co, Ni, Cu, Zn, and V, usually present as oxidized or partially oxidized metals before being reduced under hydrogen to impart or increase catalytic activity. The reduced state of these materials should to be maintained to preserve catalytic activity.

An additional benefit of the first catalyst bed of an oxidation catalyst is that during startup, the first bed can be used to help heat the rest of the reactor up to operating temperature. A deliberate injection of a small, controlled amount of oxygen or air, along with fuel and optionally steam, produces local heating of the bed while reducing the oxygen before it flows into the reduced catalyst part of the reactor. If needed, an ignition source for this oxygen-containing mixture could be supplied to initiate the reaction.

Testing oxidation catalysts for these uses is straightforward. First, the oxygen sensitivity of a reduced reforming or shift catalyst is determined. For example, a bed or monolith of the material to be tested is exposed to the fuel or reformate to be used in the bed. Exposure should be at a temperature, space velocity and composition selected to properly model the full-scale reactor. Then operating stability of the reduced catalyst over a reasonable time is demonstrated. Next, oxygen or air is added to the feed at a known rate, and the rate of oxygen addition is adjusted so that the catalyst is deactivated in a reasonable period of time, for example an hour.

Next, a candidate oxidation catalyst, preferably an oxidation catalyst that is also suitable for performing reforming or the water-gas shift, is selected. An amount of this catalyst is placed in front of the reduced catalyst bed, and its effect on the time to deactivation of the reduced catalyst in the presence of oxygen is determined. Then the amount of catalyst is reduced or increased until there is an appropriate amount of catalyst, or bed length, etc., to indefinitely maintain the reduced catalyst in a fully operative state. It is often helpful to estimate or to model the required amount and bed shape, based on known properties of the catalyst to be tested, to minimize experimentation. In this manner, suitable oxygen-consuming catalysts,

and their preferred configurations, can be rapidly determined by an engineer or technician.

While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

CLAIMS

What is claimed is:

1. A catalyst system comprising:

a first catalyst bed in fluid communication with a reactant feed, the first catalyst bed comprising a first catalyst that catalyzes an oxygen-consuming reaction in the reactant feed, the first catalyst being present in an amount sufficient to remove substantially all oxygen from the reactant feed before the feed exits the first catalyst bed; and

a second catalyst bed configured to receive the feed from the first catalyst bed, the second catalyst bed comprising an oxygen-sensitive catalyst that promotes a hydrogen-producing reaction in the reactant feed.

2. The catalyst system of Claim 1, wherein the hydrogen-producing reaction is a steam reforming reaction.

3. The catalyst system of Claim 1, wherein the hydrogen-producing reaction is a water gas shift reaction.

4. The catalyst system of Claim 1, wherein the first catalyst bed and the second catalyst bed are enclosed in a common housing.

5. The catalyst system of Claim 1, wherein the first catalyst comprises an oxidation catalyst.

6. The catalyst system of Claim 5, wherein the oxidation catalyst comprises a noble metal.

7. The catalyst system of Claim 6, wherein the oxidation catalyst comprises at least one noble metal selected from Ru, Rh, Pd, Ir, Au and Pt.

8. The catalyst system of Claim 1, wherein the oxygen-sensitive catalyst comprises a reduced catalyst.

9. The catalyst system of Claim 8, wherein the reduced catalyst comprises a transition metal.

10. The catalyst system of Claim 8, wherein the reduced catalyst comprises at least one metal selected from Cr, Mn, Fe, Co, Ni, Cu, Zn, and V.

11. The catalyst system of Claim 1, wherein the ability of the oxygen-sensitive catalyst to promote a hydrogen-producing reaction in the reactant feed is diminished by exposure to oxygen.

12. An improved reforming bed for economically extending the operating life of a reduced catalyst used for at least one of steam reforming and the water gas shift, the improved bed comprising a first, upstream catalyst bed containing an oxidation catalyst and a second, downstream catalyst bed containing a reduced catalyst that is used for at least one of steam reforming and the water gas shift.

13. The reforming bed of Claim 12 wherein each of a reduced steam reforming catalyst and a reduced water gas shift catalyst is preceded by a bed of oxidation catalyst.

14. The reforming bed of Claim 12 wherein the oxidation catalyst is selected to be an oxygen-tolerant catalyst that performs the same reaction as the bed that it protects, the reaction being selected from steam reforming and the water gas shift.

15. The reforming bed of Claim 12 wherein the oxidation catalyst is an ATR-type catalyst suitable for at least one of autothermal reforming and partial oxidation.

16. A method of producing a hydrogen-containing reformate from a reactant feed, comprising:

flowing the reactant feed over a first catalyst bed containing a first catalyst that catalyzes an oxygen-consuming reaction in the reactant feed to remove substantially all oxygen from the reactant feed before the feed exits the first catalyst bed; and

flowing the reactant feed over a second catalyst bed containing an oxygen-sensitive catalyst that catalyzes a hydrogen-producing reaction to produce a hydrogen-containing reformate.

17. The method of Claim 16, wherein the hydrogen-producing reaction is a steam reforming reaction.

18. The method of Claim 16, wherein the hydrogen-producing reaction is a water gas shift reaction.

19. The method of Claim 16, further comprising flowing oxygen over the first catalyst bed to promote a heat-producing reaction.

20. The method of Claim 19, further comprising permitting the heat-producing reaction to heat the second catalyst bed.

21. The method of Claim 16, wherein the first catalyst comprises an oxidation catalyst.

22. The method of Claim 21, wherein the oxidation catalyst comprises a noble metal.

23. The method of Claim 22, wherein the oxidation catalyst comprises at least one noble metal selected from Ru, Rh, Pd, Ir, Au and Pt.

24. The method of Claim 16, wherein the oxygen-sensitive catalyst comprises a reduced catalyst.

25. The method of Claim 24, wherein the reduced catalyst comprises a transition metal.

26. The method of Claim 24, wherein the reduced catalyst comprises at least one metal selected from Cr, Mn, Fe, Co, Ni, Cu, Zn, and V.

27. The method of Claim 16, wherein the ability of the oxygen-sensitive catalyst to promote a hydrogen-producing reaction in the reactant feed is diminished by exposure to oxygen.

28. A method for extending the operating life of a reduced catalyst used in the production of hydrogen, the reduced catalyst being used for at least one of steam reforming and the water gas shift, the method comprising placing an oxidizing catalyst in a first bed, the first bed being upstream of a second bed containing the reduced catalyst, so that the first bed can remove any oxygen present in a feed before the oxygen can reach the reduced catalyst.

29. The method of Claim 28 wherein the oxidation catalyst is suitable for catalyzing at least one of autothermal reforming and partial oxidation.

30. The method of Claim 28 wherein the oxidation catalyst comprises a noble metal.

31. The method of Claim 28 wherein the oxidation catalyst comprises at least one noble metal selected from Ru, Rh, Pd, Ir, Au and Pt.

32. The method of Claim 28 wherein the reduced catalyst comprises a transition metal.

33. The method of Claim 28 wherein the reduced catalyst comprises at least one metal selected from Cr, Mn, Fe, Co, Ni, Cu, Zn, and V.

34. The method of claim 28 wherein oxygen is admitted to said first bed to generate heat during startup of a reformer.

35. The method of Claim 28 wherein the first bed is heated by an external source to enhance its catalytic activity.

36. The method of Claim 28 wherein the amount of catalyst in the first bed is sufficient to protect the second bed under anticipated operating conditions.

37. The method of Claim 28 wherein the physical form of a catalyst is at least one of pelleted, granular, and monolithic.

38. The method of Claim 28 wherein the first bed is present before a second catalyst used in a shift reaction and after a third bed containing catalyst used in a reforming reaction.

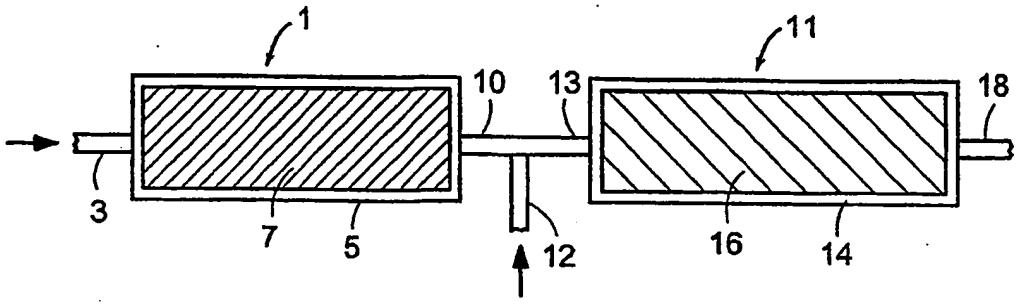


FIG. 1A

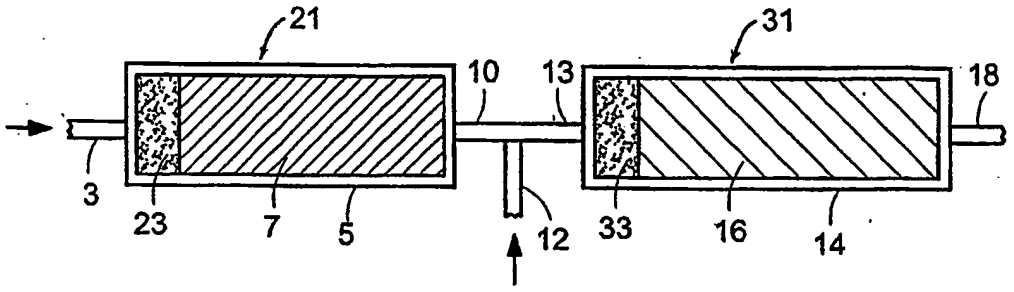


FIG. 1B

INTERNATIONAL SEARCH REPORT

International application No
PCT/US03/07232

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J23/06 B01J23/34 B01J23/38 C01B3/40 C01B3/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C01B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 02 18269 A (ENGELHARD CORP) 7 March 2002 (2002-03-07) page 6, line 28 -page 7, line 23 page 9, line 17 - line 25; figure 1 --- -/--	1-38

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
2 July 2003	29. 07. 2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	INGRID GRUNDFELT/JA A

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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